Plasma-Based Approach to Controlling the Oxygen Concentration in Graphene Oxide

S.G. Walton, E.H. Lock, and M. Baraket, Plasma Physics Division, Naval Research Laboratory, Washington, DC; P.E. Sheehan and Z. Wei, Chemistry Division, Naval Research Laboratory, Washington, DC; and J.T. Robinson and E.S. Snow, Electronics Division, Naval Research Laboratory, Washington, DC

ABSTRACT

Graphene and graphene oxide have attracted widespread interest because of their unique structural and electronic properties, which lend themselves well to the production of nanoscale electronic and sensing devices. Indeed, graphene is a single monolayer thick carbon sheet with remarkably high electron mobility. The addition of oxygen increases the sheet thickness and decreases this mobility and, more interestingly, determines both the conducting and reactive properties of the material. One significant impediment to realizing the potential of graphene oxide is the development of an industrially viable approach to producing large area substrates of well-controlled oxygen concentration. In this respect, plasmas are an ideal candidate but problems associated with the large fluxes of energetic ions are a significant concern. The Naval Research Laboratory has developed a plasma processing system that is characterized by a uniquely low incident ion energy, in the range of a few eV, at or near the carbon-carbon and carbon-oxygen bond strength. In this paper, we discuss the use of this system to reduce the oxygen concentration of graphene oxide thin films. We examine both the processing conditions and the resulting properties of the material.

INTRODUCTION

Graphene is a single monolayer thick, sp^2 carbon sheet characterized by a remarkably high electron mobility. This and other desirable qualities, have lead many to champion graphene as the material of choice for a wide variety of next-generation electronic and sensing devices. Unfortunately, producing usable quantities of graphene is problematic. This has led to the development of several processes to produce materials with graphene-like properties. One such material is graphene-oxide, which has been shown to have electronic [1] and mechanical [2] properties approaching that of graphene. The electro-mechanical differences between graphene and graphene oxide depend on the amount of oxygen present. Accordingly, processes aimed at oxygen reduction are a current research interest and wet chemical methods have been successful. Methods using hydrazine (N_2H_4) [1] or sodium borohydride ($NaBH_4$) [3] as reducing agents have been developed. Although successful, these wet chemical approaches have drawbacks as scalable production methods. First, both are time consuming (several hours). Hydrazine is toxic and leaves C-N groups on the surface, which may lead to higher than desireable resistance [3]. While sodium borohydride is safe and doesn't produce C-N groups, it is still time consuming.

Gomez [1] and co-workers have demonstrated the use of plasmas as a reducing method. In this work, graphene oxide was exposed to a low power (30W), high pressure (600 mTorr) hydrogen plasma for 5-10 seconds. The rGO had electronic properties that were comparable to chemically reduced GO.

Plasma-based processes are an attractive replacement for chemical methods given that they are largely environmentally benign, fast, and are amenable to device fabrication given the large infrastructure that exists. For the processing of ultra-thin films however, great care must be taken not to damage the films. Indeed, high etch rates are not desirable for films on the order of several monolayers thick. With this in mind, the incident ion energy often present in discharge plasmas can be problematic.

The Naval Research Laboratory has developed a materials processing system based on electron beam-generated plasmas for use in a range of applications [4]. When high-energy ($\approx$ 2 keV) electron beams are used as the primary ionization source, the resultant plasmas have several unique characteristics when compared to conventional low-pressure plasma sources. Relevant to this work is the very low electron temperatures. In beam produced plasmas, the electron temperature varies with the working gas, but is $\leq$1 eV [5] in all gases and the accompanying ion kinetic energies are less than 5 eV [6]. In discharges, the electron temperature is typically above 2 eV and so the minimum energy is at least twice that in electron beam generated plasmas. This low incident ion energy is attractive in that etching should be minimal. This has been demonstrated in the use of these plasmas to modify polymers [7]. It is with this in mind, that we have investigated the use of these plasmas in the reduction of graphene oxide.

EXPERIMENTAL

The processing apparatus has been discussed previously [8] and is shown in the schematic of Figure 1. The system vacuum was maintained by a 250 l/s turbo pump, with a base pressure on the order of 10^{-7} Torr. The operating pres-

© **2009 Society of Vacuum Coaters** 505/856-7188

52nd Annual Technical Conference Proceedings, Santa Clara, CA, May 9–14, 2009 ISSN 0737-5921

sure was achieved by introducing high-purity gases through mass flow controllers and throttling the turbo pump using a manual gate valve.

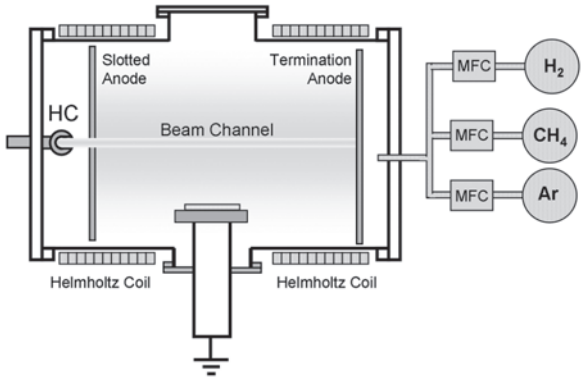

Figure 1: A schematic diagram of the processing system.

The electron beam was produced by applying a 1.6 kV pulse to a linear hollow cathode for a selected pulse duration and duty. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further downstream. The electron beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1 cm x 25 cm) and the anode-to-anode length (40 cm). Beam spreading from collisions with the neutral background was largely eliminated by a co-axial magnetic field (150 Gauss) that was produced by a set of external magnetic field coils.

For processing, plasmas were produced in backgrounds of pure Argon, Argon/hydrogen mixtures and argon/methane mixtures. For the mixtures, hydrogen and methane were fixed at 10% by flow. The total pressures ranged between 30 and 90 mTorr.

Graphene oxide was spin cast on Si wafer using the method described in [9]. The thin film thickness was in the range of 10-20 nm. Pre- and post-processing surface diagnostics included xps and surface energy measurements. Chemically reduced graphene oxide was also produced for use as a comparison to the plasma reduced graphene oxide. Chemical reduction was carried out via exposure to hydrazine hydrate, also described in [9].

RESULTS AND DISCUSSION

Initially, graphene oxide was exposed an argon plasma to determine the physical changes to the surface. In argon, ion kinetic energies are expected to be on the order of a few eV [6]. Accordingly, little material removal was expected and verified. The addition of any molecular gas to the background will reduce the electron temperature and thus decrease the ion energies [6]. More importantly, the addition of hydrogen containing gases is expected to promote chemical reactions that lead to the removal of oxygen. A comparison of reductions carried out in the various gas mixtures is shown in Figure 2. In all cases, the total operating pressure was 50 mTorr. For comparison, Highly Oriented Pyrolytic Graphite (HOPG) is included in all results.

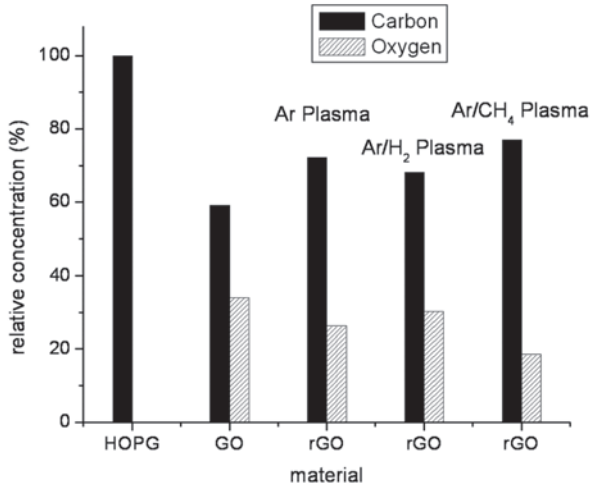

Figure 2: Chemical composition of the various materials including Highly Oriented Pyrolytic Graphite (HOPG), as-received graphene oxide (GO) and plasma reduced graphene (rGO). The operating pressure for all gas mixtures was 50 mTorr.

The best results, in terms of reducing the amount of oxygen present in graphene oxide, were accomplished using plasma produced in mixture of argon and methane. Interestingly, the use of plasmas produced in mixtures of argon and hydrogen was least effective. The reasons for this are unknown but remain an active area of interest.

For plasmas produced in mixtures of argon and methane, additional experiments were performed and it was found that higher operating pressure lead to an even greater reduction in the relative concentration of oxygen in rGO. The results of Figure 3 show a comparison between chemically reduced graphene oxide (using hydrazine hydrate) and plasma reduced graphene oxide in a 90 mTorr gas mixture containing 10% methane.

Of interest is the ability to achieve similar oxygen concentration using the plasmas approach as compared to the chemical approach. As significant is the absence of nitrogen in the plasma reduced GO. It has been suggested that the presence of nitrogen in rGO can cause higher sheet resistances than graphene oxide of comparable oxygen concentrations [3].

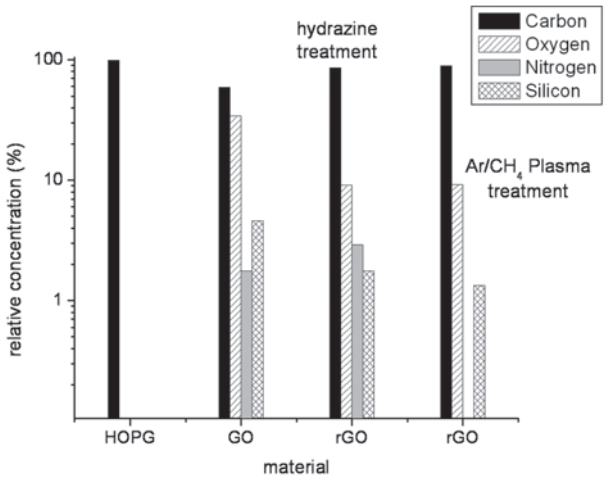

Figure 3: Relative chemical concentrations of as-received materials, chemically reduced GO, and plasma reduced GO. The plasma was produced in 90 mTorr mixture of argon and methane (10%).

As expected, a reduction in the amount of oxygen present in graphene oxide reduces the surface energy and makes the surface more hydrophobic (see Figure 4). Given the similar oxygen concentrations in chemically and plasma rGO, the surface energies are the same. Interestingly, the values are nearly identical to that of HOPG.

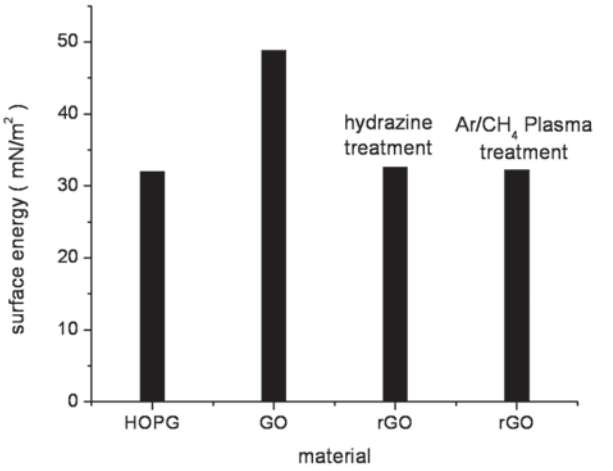

Figure 4: Surface energies of as-received materials, chemically reduced GO, and plasma reduced GO. The plasma was produced in 90 mTorr mixture of argon and methane (10%).

CONCLUSION

A reduction in the relative concentration of oxygen present in graphene oxide using plasma produced in mixtures of argon and methane. The results indicate the process is able to achieve the same results as reduction via wet chemistry. The amount of time required to achieve plasma reduction is on the order of seconds as compared to hours using wet chemical approaches. Moreover, the process is easily scaleable to accommodate large scale, thin films. Both are desirable in the fabrication of devices and certainly needed to make graphene-based devices economically viable.

ACKNOWLEDGEMENTS

This work is supported by the Office of Naval Research. EHL, MB and ZW appreciate the support of the National Research Council.

REFERENCES

1. C. Gomez-Navarro, R.T. Weitz, A.M. Bittner, M. Scolari, A. Mews, M. Burghard, and K. Kern, "Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets," *Nano Lett.* 7(11), 3499 (2007).

2. C. Gomez-Navarro, M. Burghard, and K. Kern, "Elastic Properties of Chemically Derived Single Graphene Sheets," *Nano Lett.* 8(7), 2045 (2008).

3. H.-J. Shin, K.K. Kim, A. Benayad, S.-M. Yoon, H.K. Park, I.-S. Jung, M.H. Jin, H.-K. Jeong, J.M. Kim, J.-Y. Choi, and Y.H. Lee, "Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance," *Adv. Funct. Mater.*, 19, 1 (2009).

4. D. Leonhardt, S.G. Walton, and R.F. Fernsler, "Fundamentals and applications of a plasma-processing system based on electron-beam ionization," *Phys. Plasmas* 14, 057103 (2007).

5. E.H. Lock, R.F. Fernsler, and S.G. Walton, "Experimental and theoretical evaluation of electron temperature in electron beam generated plasmas," *Plasma Sources Sci.* Technol. 17, 025009 (2008).

6. S.G. Walton, C. Muratore, D. Leonhardt, R.F. Fernsler, D.D. Blackwell, and R.A. Meger, "Electron beam-generated plasmas for materials processing," *Surf. Coat. Technol.*, 186(2), 40 (2004).

7. E.H. Lock, S.G. Walton, and R.F. Fernsler, "Physio-Chemical Modifications of Polystyrene and Poly(propylene) Surfaces by Electron Beam-Generated Plasmas Produced in Argon," *Plasma Proc. and Poly.* 6, 234-245 (2009).

8. S.G. Walton, E.H. Lock, D. Leonhardt, and R.F. Fernsler, "Electron Beam-Generated Plasmas for Polymer Surface Modification," *50th Annual Technical Conference Proceedings of the Society of Vacuum Coaters*, pp 125-128, 2007.

9. J.T. Robinson, M Zalalutdinov, J.W. Baldwin, E.S. Snow, Z Wei, P. Sheehan, and B.H. Houston, "Wafer-scale reduced graphene oxide films for nanomechanical devices." *Nano Lett.* 8(10), 3441 (2008).